Conformational behavior of polymers adsorbed on nanotubes

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The importance of hydrophobic interactions in determining polymer adsorption and wrapping of carbon nanotubes is still under debate. In this work, we concentrate on the effect of short-ranged weakly attractive hydrophobic interactions between polymers and nanotubes (modeled as an infinitely long and smooth cylindrical surface), neglecting all other interactions apart from chain flexibility. Using coarse-grained Monte Carlo simulation of such simplified systems, we find that uniform adsorption and wrapping of the nanotube occur for all degrees of chain flexibility for tubes with sufficiently large outer radii. However, the adsorbed conformations depend on chain stiffness, ranging from randomly adsorbed conformations of the flexible chain to perfect helical or multihelical conformations (in the case of more concentrated solutions) of the rigid chains. Adsorption appears to occur in a sequential manner, wrapping the nanotube nearly one monomer at a time from the point of contact. Once adsorbed, the chains travel on the surface of the cylinder, retaining their helical conformations for the semiflexible and rigid chains. Our findings may provide additional insight to experimentally observed ordered polymer wrapping of carbon nanotubes.


I. INTRODUCTION

There is increasing evidence that shows that various types of polymers can be used to solubilize carbon nanotubes (CNTs), under either aqueous or organic solvents, by wrapping around the surface of the nanotube in a highly ordered monolayer. These materials are believed to efficiently coat the surface of the CNTs through physical interactions, overcoming the strong van der Waals attraction between the tubes. Further evidence reveals that nanotubes with a narrow range of diameters are most readily solubilized, presumably due to strong interactions with the polymers. Following these findings, several postulates emerged as to the main driving force for solubilization of CNTs using noncovalent adsorption of polymers. In particular, wrapping of polymers containing aromatic groups on the backbone or side chains has been frequently attributed to \( \pi \)-stacking interactions with the graphite surface of the tube. Such mechanism was also confirmed by molecular dynamics (MD) simulations. However, other MD studies found van der Waals (vdW) forces to be the dominant drive for adsorption and wrapping of polymers on CNTs.

Interestingly, an extensive set of experiments on various types of polymers and in various types of solvents, carried out by Baskaran et al., suggests that polymer wrapping of CNTs is a universal phenomenon, determined largely by a strong drive for adsorption in aqueous media and by weak hydrophobic interactions in organic solvents. An increasing number of atomistic and coarse-grained simulation studies also support helical wrapping of polymers around CNTs. Here, too, there is conflicting evidence that supports either the role of \( \pi-\pi \) stacking, or nonspecific vdW attraction (even for complex biomacromolecules), in determining the preferred wrapping conformation.

The observation that ordered (often helical) wrapping of nanotubes may be a general phenomenon is also supported by studies of isotropic polymer systems under various entropic constraints that predict the presence of ordered conformations. For example, steric and excluded volume effects have shown to lead to helical conformations in polymers, and a stable toroidal state was also shown to exist for stiff polymers at low temperatures. Similarly, a study by Maritan et al. on the optimal shape of a string of fixed arc length confined in a finite box indicates that conditions exist for which particular pitch-to-radius helix ratios are preferred. These studies provide an intuitive basis for anticipating helical conformations of semiflexible polymers confined to a cylindrical surface. However, the mechanism of adsorption and formation of helical wrapped conformations around such curved surfaces remains unclear.

While it has long been accepted that long flexible chains interacting with mesoscopic particles exhibit universal behavior which depends on the shape of the particles and is independent of the microscopic chemical detail of the system, it is less intuitive that similar universality may be found on nanoscale dimensions. Early theoretical studies that treated explicitly the problem of polymer adsorption on cylindrical surfaces and other mesoscopic particles considered Gaussian chains, which do not display helical wrapping behavior. However, theoretical models for the adsorption of charged helical chains on an oppositely charged cylinder did reveal the presence of helical conformations, whose pitch depends on the competition between electrostatic energy and chain persistence length. As with ordered polymer wrapping of CNTs, these studies suggest that helical and other
ordered conformations, which are induced by isotropic interactions that limit the configurational space of the polymer, are a general phenomenon of polymers, and may be in direct competition with specific interactions such as π-stacking interactions or ordered adsorption driven by helical biopolymers.  

Recently, using a coarse-grained Monte Carlo simulation of hard sphere chains confined to a cylindrical surface, we observed stable helical conformations at a narrow range of cylinder radii. This problem corresponds to the strong adsorption limit such as that of polymer-CNT interaction in an aqueous solvent. While flexible chains were found to exhibit random (nonhelical) wrapping conformation, rigid polymers adopted nearly perfectly helical conformations. The conformation of the semiflexible chain was found to strongly depend on cylinder radius, with linear nonwrapping conformations at small radii, and helical conformations at intermediate cylinder radii. In the case of a weakly attractive surface (e.g., hydrophobic interactions in an organic medium), we did not observe linear adsorbed conformations at small radii. However, we found that the presence of vdW attraction between monomers leads to adsorbed conformation in the form of multiple helices.

In this work, we further analyze the role of weakly attractive interactions on the conformational behavior and adsorption of a dilute solution of semiflexible polymers on a smooth cylindrical surface. We concentrate on the adsorption transition and mechanism of helical wrapping, evaluating mechanisms that lead to adsorbed ideality and the formation of multiple helices. In the following section, we briefly discuss the simulation model introduce in Ref. 17. In Sec. III, we present and discuss our results, focusing on the “dynamics” of adsorption and helical wrapping. We offer concluding remarks in Sec. IV.

II. METHODOLOGY

In this section, we briefly describe the coarse-grained Monte Carlo (MC) simulation model we developed to study polymer behavior near a nanotube. Details of the simulation are described elsewhere.  

We utilize a minimalist model in order to concentrate on the physical effects that drive long polymer chains to adsorb on the surface of the cylinder and adopt ordered conformations. The monomers are modeled as soft spheres interacting via the Lennard–Jones potential,

\[ U_{lj}/kT = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right], \]

where \( k \) is the Boltzmann constant, \( T \) is the temperature, \( \epsilon \) is the two-body Lennard–Jones interaction parameter, \( \sigma \) is the effective monomer size, and \( r \) is the distance between two interacting nonbonded monomers. A cutoff radius of \( 2^{1/6} \sigma \) was used to concentrate on the effect of short-range attractive forces.

Chain stiffness, which plays a central role in determining chain conformational behavior, is described by the following harmonic expression for the energy required to bend the angle \( \theta \) formed between three consecutive monomers from 180°,

\[ U_j/kT = \kappa (\cos \theta - 1)^2, \]

where \( \kappa \) characterizes the resistance of the bond angle \( \theta_j \) about monomer \( j \) to bending. \( \theta_j \) is defined by \( \cos \theta_j = \mathbf{b}_{j+1} \cdot \mathbf{b}_j / (|\mathbf{b}_{j+1}| |\mathbf{b}_j|) \), where \( \mathbf{b}_j = r_{j+1} - r_j \). The bending stiffness parameter \( \kappa \) appearing in Eq. (2) can be easily related to the persistence length \( l_p \) through a bond angle correlation function, which decays exponentially with \( l_p \), thereby obtaining a power law dependence of \( l_p \) on \( \kappa \).

The nanotube is modeled as a smooth infinitely long cylindrical shell with a continuous Lennard–Jones (LJ) potential field averaged over the tube length. The polymer-tube interactions are obtained by integrating the dimensionless LJ potential over the length of the tube in order to obtain a potential that depends on tube dimensions (inner radius \( R_i \) and outer radius \( R_o \)) and the perpendicular distance of a monomer from the surface of the tube, \( D \),

\[ U_{cyt}(R_i, R_o, D) = 8\pi\epsilon_w \int_0^{2\pi} d\phi \int_{R_i}^{R_o} \rho d\rho \left( \frac{63}{512 \chi^{3/2}} - \frac{3}{16\chi^{5/2}} \right), \]

where \( \epsilon_w \) is the tube–monomer LJ interaction parameter and \( x = (D + R)^2 + \rho^2 - 2\rho(D + R)\cos \varphi \). The integration over \( \varphi \) and \( \rho \) is performed numerically once at the beginning of the simulation for each of the outer radii considered. A tube thickness of 1\( \sigma \) was considered in all our calculations, and \( \epsilon_w \) was adjusted such that the potential minimum of tubes of different radii corresponds to the potential minimum of a tube with \( R_o = 2\sigma (\epsilon_w, \text{min} = -1.46) \) in order to concentrate on the effect of surface curvature. This value of \( \epsilon_{w,\text{min}} \) is slightly lower than the potential minimum, \( \epsilon_{\text{min}} = -1 \), taken for monomer–monomer interactions. The potential cutoff of \( U_{cyt} \) was taken at 2\( \sigma \).

Simulations were carried out on chains consisting of 100 monomer units. A cubic simulation box (100\( \sigma \times 100\sigma \times 1000\sigma \)) with periodic boundary conditions was considered with the nanotube placed in the center of the box. The chains (from a single chain up to ten chains) were initially placed randomly within the box. Equilibration was achieved using a combination of reptation and kink-jump moves, tried with approximately 0.6 and 0.4 probabilities, respectively. This choice corresponds to an average Metropolis acceptance rate of about 50\%. To ensure equilibration, 10\(^6\) MC steps were performed prior to calculating average properties. Averages were calculated over an additional 10\(^7\) MC steps, sampled every 10\(^5\) MC steps.

As we have previously reported, there exists a range of parameters of tube radii for which semiflexible chains show ordered adsorbed behavior. In addition, we presented evidence that points to an adsorption transition followed by a sharp order transition to nearly perfect helices as chain stiffness is increased. In the following section, we analyze the nature of these transitions and relate them to the conformational behavior of the adsorbed chains.
III. RESULTS AND DISCUSSION

A. Adsorption

Although our MC simulations do not present the true dynamics of the adsorption process, we can qualitatively observe several features. Simulation snapshots, depicted in Fig. 1 [for flexible chains (top) and for rigid chains (bottom)], suggest that adsorption of each chain occurs sequentially. Chains eventually diffuse to the surface, and adsorption proceeds in a sequential manner, essentially one monomer at a time from the initial point of contact with the cylinder. The flexible chains adsorb in clouddlike conformations, but nonetheless, once adsorbed they remain adsorbed for the remainder of the simulation. At the concentrations studied, we seldom observe overlap between the adsorbed flexible chains due to their sterically hindered random conformations. The semiflexible and rigid chains, on the other hand, wrap in a helical manner around the surface of the nanotube. The helical pitch and periodicity depend on chain stiffness and tube diameter (discussed below). As with the flexible chains, the rigid chains remain confined to the surface of the cylinder for the remainder of the simulation, however, these chains gain entropy by weaving in and out of neighboring adsorbed chains, thereby forming multiple helices for significant periods of the simulation run.

In order to follow the positioning of the chains relative to the surface of the tube during the course of the simulation, we calculated the contributions from the parallel and perpendicular components of the center of mass (COM) of each chain relative to the surface. The perpendicular contribution, \( \text{COM}_{\perp} \), gives an indication of the average distance of each chain from the surface of the tube. Moreover, \( \text{COM}_{\perp} < R_g \) for wrapping conformations, since the surface is impenetrable. This inequality is exact if the chains adsorb in an ideal helix, and is approximate for conformations that deviate from the ideal helix, and do not evenly wrap around the tube. The parallel contribution, \( \text{COM}_p \), allows us to follow the average position of the chain in the direction parallel to the cylinder axis, providing an indication of surface diffusion. A sample plot of the COM components for flexible and rigid chains is shown in Fig. 2, where each curve in the figures corresponds to the COM of a single chain in a three-chain system. We observe that both rigid and flexible chains adsorb quite quickly, displaying quite a sharp decrease in \( \text{COM}_{\perp} \). Furthermore, once adsorbed the chains remain so for the remainder of the simulation. Moreover, despite the higher drive for adsorption of the semiflexible chain (due to the lower entropic penalty upon adsorption) and their more extended conformations, we observe that the flexible chains adsorb more quickly, presumably due to their higher diffusivity.

The parallel and perpendicular components of the diffusivity of the COM of the chains, \( D_p \) and \( D_{\perp} \), can be used to quantify the mobility of the chains as adsorption proceeds relative to the surface of the tube. The components of the diffusivity were calculated from

\[
D_x = \frac{\sum_{i=1}^{n} (\text{COM}_{x,i} - \text{COM}_{x,i-1})^2}{\Delta t},
\]

where the subscript \( x \) denotes either the parallel (\( || \)) or perpendicular (\( \perp \)) component and \( \Delta t \) is the simulated time. In Fig. 3, we show the average diffusivity of the COM of an adsorbing chain as a function of MC cycles. Prior to adsorption, both diffusivities in the direction parallel (\( D_p \)) and in the direction perpendicular (\( D_{\perp} \)) to the cylinder axis are reasonably high. Once adsorption occurs, \( D_{\perp} \) decreases substantially and remains low for the adsorbed chain. \( D_p \) essentially retains its initial values, providing another indication that the adsorbed chains are quite mobile even when adsorbed on the surface of the cylinder. As anticipated, the rigid chain (red curves) shows similar trends of \( D_p \) and \( D_{\perp} \), but with overall lower diffusivity when compared with the flexible chain.

B. Conformational properties

The persistence length of the chain, which depends on bond angle stiffness, plays a significant role in determining the adsorption behavior. There appears to be a transitional tube radius and chain stiffness beyond which essentially full adsorption of LJ chains from dilute solution is observed.\(^{13}\) The adsorbed fraction as a function of cylinder radius for different values of \( \kappa \) is shown in Fig. 4. We note again that the cylinder LJ potential was adjusted, such that the attractive energy at the minimum corresponds to that of a cylinder with \( R_c = 2\sigma \), for all cylinder radii to eliminate the effect of surface attraction and concentrate on the effect of geometry. Figure 4 suggests that there is a minimum cylinder radius for which fully adsorbed and ordered wrapping conformations prevail. That is, at small tube radii (below \( 2\sigma \)), the sharply curved surface prevents adsorption due to the high energetic (bending) and entropic (topological) costs, while at large radii, randomly oriented conformations result, similar to adsorption on a flat surface. The regime around \( \rho = 1\sigma \) exhibits distinguished behavior from other radii, and is manifested by a peak in energy fluctuations.

While the effects of surface curvature may be anticipated based on previous studies of similar systems,\(^{8,15,16,24,25}\) the change of conformational behavior with \( \kappa \) displays addi-
tional details. In a previous communication, we reported our results on the helical correlation length obtained from the following expression:

\[ G(m) = \exp(-m/\xi)\cos(2\pi m/P), \]

where \( G(m) \) describes the helical correlation between two chain units at a contour distance \( m \), and \( P \) is the periodicity of the helical turn (i.e., the average number of segments per helical turn). Equation (5) is an empirical fit to a calculated function \( G'(m) \) that quantifies the bond angle correlation. \( G'(m) \) is essentially the covariance of cosines of the bond angle about monomer \( i \) and fictitious bond angles between bond vector \( i \) and the vector connecting monomer \( i \) to monomer \( j \) that is \( m \) contour units away. \( G'(m) \) is then averaged over all relevant monomers along the contour of the chain.
A fit of $G'(m)$ to Eq. (5) can then be used to quantitatively describe the helical periodicity $P$ and its decay $\xi$. At its extremes, $\xi$ approaches chain length for a perfect helix, and $\xi \to 0$ for nonhelical conformations, displaying an exponential decay with no oscillations.

The correlation length $\xi$ and the periodicity $P$ were evaluated for different values of $\kappa$ and $\rho$. $\xi$ shows interesting dependence on $\kappa$, as can be seen in Fig. 5 for $R_o=2\sigma$ (similar results are observed for other tube radii). At small values of $\kappa$, there is intuitively little correlation between the segments in the adsorbed state. For large $\kappa$, polymers appear to adsorb in nearly perfect helices, with $\xi$ approaching chain length. In this case, we expect a simple linear decrease in $1/\xi$ with increasing $R_o^2$ (see illustration in Fig. 6) due to the following relation:

$$p^2 + (2\pi R_{\text{eff}})^2 = \left(\frac{L}{N_t}\right)^2,$$

where $p$ is helical pitch and $R_{\text{eff}}$ is the distance at the potential minimum of $U_{\text{cyt}}$. For example, for $\kappa=50$, we obtain a pitch of approximately 15$\sigma$. In Fig. 7, we show the linear relation found between the average number of turns ($N_t$) and cylinder radius. The transition between these two extremities of $\kappa$ appears to occur in two clear steps, at $\kappa \sim 5$ and $\kappa \sim 40$ (the value of $\kappa$ at the transition varies somewhat with cylinder radius). Interestingly, these values correspond approximately to the flexible and rigid limits, respectively, of the semiflexible polymer regime, as predicted by the Kratky–Porod wormlike chain model,31 shown in Fig. 8. Comparison of the initial increase in $\xi$ with the adsorption fraction (Fig. 4) and the transition from the flexible to the semiflexible limit (Fig. 8) suggests that this relatively sharp increase is related to the transition to nearly full adsorption characterizing semiflexible and rigid chains. As chain rigidity increases from the semiflexible to rigid regime, we observe a linear increase in the helix correlation length, followed by a second sharp transition of $\xi$ with $\kappa$, indicative of a conformational transition to nearly perfect helical adsorbed states.

This two-step transition is further corroborated by the fluctuations in adsorbed fraction and energy per segment as a function of $\kappa$, shown in Fig. 9. The peak in the fluctuations of adsorbed fraction demonstrates a transition from weak to strong adsorption at low values of $\kappa$. Energy fluctuations are characterized by two distinct peaks; one following the adsorption transition and another at around $\kappa=40$. These results

![FIG. 5. Change of helical correlation length $\xi$ with chain rigidity $\kappa$. $R_o=2\sigma$ and $N_t=2$.](image)

![FIG. 7. Relation between the average number of turns and cylinder radius. $\kappa=50$, $R_o=2\sigma$, and $N_t=2$.](image)

![FIG. 6. Schematic depiction of a helical chain configuration on an unfolded cylinder surface.](image)

![FIG. 8. (Color online) Normalized end-to-end distance vs number of persistence units $n_p=L/l_p$. Prediction of Kratky–Porod wormlike chain model (Ref. 31) (solid curve) and our MC simulations (circles, different shades represent chains of different contour length $L$), respectively. The limits of the rigid rod regime at low values of $L/l_p$ ($\langle R^2 \rangle^{1/2} \sim N^1$) and flexible regime ($\langle R^2 \rangle^{1/2} \sim N^{1/2}$) at high values of $L/l_p$ are shown by the thin solid lines. The arrows indicate the values of $\kappa$ corresponding to the transitions observed in the helical correlation length.](image)
suggest that the adsorption transition is accompanied by conformational rearrangement to the more entropically favored wrapping conformations, which allows for chain diffusivity on the surface. A second conformational transition characterizes the transition from semiflexible to rigid chains, the latter of which adopt nearly perfect helical conformations.

C. Polymer concentration

As suggested in the simulation snapshots of Fig. 1, increasing the chain concentration leads to overlap between the adsorbed chains, and for sufficiently high $\kappa$ results in the formation of multiple helices. In Fig. 10 we show the change in surface coverage (number of monomers per unit area of cylinder) as a function of the number of chains present in the solution. It can be seen that as chain concentration is increased, surface coverage increases linearly to a plateau, corresponding to approximately 30% coverage of the surface. Interestingly, surface coverage, in general, appears to only weakly depend on chain rigidity for sufficiently rigid chains ($\kappa > 10$). Snapshots of sample equilibrium configurations for flexible and rigid chains are shown in Fig. 11. From these snapshots, it is clear that the random conformations adopted by flexible chains (left) do not allow for significant overlap due to steric constraints, as has been intuitively postulated by O’Connell et al. The rigid chains, on the other hand, can easily accommodate higher adsorbed fractions by forming multiple helices at high concentrations (right). Interestingly, chains lacking weakly attractive interactions between monomers (i.e., $R_{cut}=1\sigma$) rarely overlap (results not shown), thereby minimizing their free energy by maximizing entropy.

D. Block copolymer adsorption

Block copolymers consisting of hydrophobic (H) and polar (P) segments have been shown to disperse CNTs in aqueous solution. The common assumption for these studies is adsorption of the hydrophobic monomers, while the polar segments extend to the aqueous solvent. We carried out preliminary simulations on block copolymer–nanotube systems, where the hydrophobic segments are attracted to the cylinder with interactions according to Eq. (1). The polar segments feel a repulsive potential equal to or greater in strength, according to

$$\frac{U_p}{kT} = 4\varepsilon \left( \left( \frac{\sigma}{r} \right)^{12} + \left( \frac{\sigma}{r} \right)^{6} \right).$$

Figure 12 presents a snapshot of our simulated diblock copolymer–nanotube system. As might be expected, a sufficiently long and stiff hydrophobic block, wraps around the tube in a helical manner, forming a hydrophobic layer on the surface, while the polar units extend to the bulk. We are currently extending our simulations to triblock HPH systems, where it is anticipated that the hydrophobic blocks will anchor the polymer onto the surface of the nanotube, while the polar block will remain extended toward the bulk in a loop. Such a conformation should increase the entanglement of the adsorbed polymers with the bulk polymers, allowing for greater reinforcement of the interface between the nanotube and polymer phase. Such a system may be useful in the tailored design of nanocomposite materials.
IV. CONCLUSIONS

We carried extensive MC simulations to study the adsorption of a dilute solution of polymers on an infinitely long cylindrical surface (nanotube). We concentrated on a simplified model in order to isolate the role of weak physical interactions on polymer wrapping around CNTs. Adsorption was found to proceed in a sequential manner, leading to significant adsorption for the duration of the simulation, even for weakly attractive surface. Consequently, adsorption leads to a drastic decrease in the diffusivity of the chains in the direction perpendicular to the cylinder axis. However, the chains retain their bulk diffusivity in the direction parallel to the cylinder axis, indicating that the chains are free to travel up and down on the surface. While the weak vdW attraction of the cylinder leads to adsorption of flexible chains (on sufficiently large radii), these chains wrap the cylinder in a “cloud” conformation, allowing them to retain high entropy by sampling a large number of conformations. However, flexible chains show negligible overlap at the range of concentrations studied. On the other hand, high polymer concentrations of semiflexible and rigid chains allow for the formation of multiple helices, which result from further optimization of the adsorbed conformations in order to maximize chain entropy and the vdW interactions between the chain segments. The presence of multiple helical conformations results in uniform monolayer coverage of the nanotube surface. In comparison, the adsorbed layer of the more flexible chains appears substantially thicker and nonuniform.

Our results strongly support the notion that wrapping of nanotubes by polymers, and more specifically helical wrapping, is a universal phenomenon of polymer behavior, which depends on cylinder radius and more importantly on chain persistence length. As such, helical wrapping can be manipulated and utilized favorably as a means to anchor polymers around nanotubes, as in the case of diblock or triblock copolymers.


